

POLISHING AGENT, METHOD OF PRODUCING SAME,  
AND METHOD OF POLISHING

Background of the Invention

5           This invention relates to a polishing agent comprised of mother particles and very fine abrading particles, and in particular to such a polishing agent comprised of mother particles on the surfaces of which very fine abrading particles are supported, as well as a method of polishing by using such a polishing agent.

10           Cloths of various kinds with free abrading particles are recently being used for the fine finishing in the production of high-tech electronic devices such as semiconductor substrates and magnetic disc substrates. In such a process, elastic cloths such as woven cloths, unwoven cloths and foamed substances are used for producing mirror surfaces. About 30 years ago, it was mostly woven cloths that were being used, but since the woven texture had adverse effects on the roughness and unevenness, they have gradually  
15           ceased to be used and unwoven cloths have come to be used mostly. Since unwoven cloths have unevenness in the density, however, it has been pointed that they also have adverse effects in the fine-scale unevenness. Thus, the use of foamed substances are now beginning to increase.

20           Recently, there is an increasing demand for processing with high precision in shape, and harder polishing cloths are coming to be favored. There are problems, however, with the use of a hard cloth such as the difficulty in achieving required roughness and the tendency to produce scratches. In view of such problems, there has also been a proposal to use a double-layered polishing cloth with a hard resin layer and a soft resin layer superposed one over the other.

25           Such prior art polishing agents and methods have many problems. Firstly, for example, the surface roughness of prior art polishing cloths becomes quickly diminished, and both scraped materials and the polishing materials become accumulated with the time of use such that the polishing efficiency is adversely affected. For this reason, the common practice is to use a diamond grinder to rework the cloth surface, which is a  
30           process referred to as the "conditioning". This process tends to shorten the useful

lifetime of the polishing cloth, and there is the problem of abrading particles dropping off from the diamond grinder and scratching the target surface being polished.

Secondly, since polishing cloths have a thickness of about 2-3mm, their elastic deformation is relatively large and they sometimes come into a direct contact themselves with the target surface, thereby increasing the frictional resistance and hence also the power consumption by the polishing machine.

Recently, furthermore, it is sometimes required to polish a surface with a large diameter and accordingly larger polishing machines are coming to be used. In order to be used on such a larger polishing machine, the size of polishing cloths is also increasing. It takes the skill of a highly experienced worker to attach a large polishing cloth uniformly over the plate of a polishing machine.

#### Summary of the Invention

It is therefore an object of the invention to provide a polishing agent and a polishing method with a durable polishing capability for an extended period of use, reducing unnecessary frictional resistance not directly contributing to the polishing and not requiring reattachment of a cloth material.

A polishing agent embodying this invention, with which the above and other objects can be accomplished, may be characterized as comprising mother particles and very fine abrading particles on the surfaces of the mother particles. These abrading particles are supported on the surfaces of the mother particles during a polishing process and, if removed from a portion of the mother particle's surface, become reattached to the surface of a mother particle. The average diameter of the abrading particles is 1/500-1/5 of that of the mother particles. Such a polishing agent can be produced by adding mother particles into a polishing liquid having the very fine abrading particles dispersed therein and by stirring the mixture.

Such an agent may be used according to a method of this invention by supplying a specified amount of the agent between a target object to be polished and a flat and smooth polishing means such as a lapping plate or a tape and causing the polishing means to undergo a motion such as a rotary motion relative to the target object for carrying out a lapping process.

By means of a polishing agent and a polishing method of this invention, an object can be polished without using a polishing pad or anything wasteful which does not directly contribute to the polishing. By a method of this invention, the polishing efficiency can be improved by 20-50% and the throughput can be increased. Moreover, the polishing machine can be miniaturized for the space-saving advantage.

#### Brief Description of the Drawings

Fig. 1 is a sectional view showing the polishing process using a polishing agent embodying this invention;

Figs. 2(a), 2(b), 2(c), 2(d) and 2(e) (together referred to as Fig. 2) show mother particles of other types according to this invention;

Figs. 3(a), 3(b), 3(c), 3(d) and 3(e) (together referred to as Fig. 3) show mother particles according to this invention in different shapes; and

Figs. 4(a), 4(b), 4(c), 4(d), 4(e) and 4(f) are photographs by electron microscope of a polishing agent embodying this invention.

#### Detailed Description of the Invention

In what follows, the invention is described with reference to the drawings. Fig. 1 is a sectional view of a polishing agent embodying this invention, having been supplied on a lapping plate 2 and being used for polishing a target object 1.

The polishing agent for polishing the surface of the target object 1 is comprised of mother particles 3 and very fine abrading particles 4 attached to the surfaces of these mother particles 3. During the polishing process, the abrading particles 4 remain supported on the surfaces of the mother particles 3. The invention is characterized wherein the abrading particles 4, if removed from the surfaces of the mother particles 3 during a polishing process, become reattached to the portions of the surfaces from which they have been removed. The average diameter of the very fine abrading particles 4 is  $1/500-1/5$ , and preferably  $1/200-1/20$ , of that of the mother particles 3.

According to a preferred embodiment of the invention, the mother particles 3 are spherical polymers and the average diameter (indicated by numeral 8) of the abrading particles 4 is  $1/500-1/5$ , and preferably  $1/200-1/20$ , of the average diameter (indicated by

numeral 6) of such spherical polymers. Since these spherical polymers are elastic, they do not leave any scratch marks on the surface of the target object 1 by a lapping process. The spherical polymers 3 according to this invention may be porous with small holes of sizes 200-1000Å.

5        Such spherical polymers may be comprised of one or more selected from urethane, nylon, polyimides and polyesters. The very fine abrading particles 4 may be comprised of one or more selected from colloidal silica, alumina and cerium oxide.

10        The spacing (indicated by numeral 5) between the target object 1 to be polished and the lapping plate 2 (which are practically in contact with each other in the sense of in a pressure-communicating relationship) is substantially equal to the average diameter 6 of mother particles 3. Empty spaces 7 between mutually adjacent pairs of the mother particles 3 serve as a pocket, preventing scratches. Polishing agents according to this invention are usable for the fine polishing of magnetic disk substrates, semiconductor wafers and liquid crystal display panels.

15        Micro-beads other than polymers as described above may also be used as the mother particles. The average diameter of micro-beads to be thus used is in the range of 0.1-300µm, and preferably 1-20µm. Such micro-beads may contain small holes of 200-1000Å. Practical examples include those containing one or more kinds selected from carbon micro-beads, glass beads, acryl beads and mesocarbon beads which are all  
20        available commercially (say, from Osaka Gas Co. and Simicon Composite Co.)

Fig. 2 shows mother particles of other types according to this invention. Figs. 2(a), 2(b) and 2(c) show examples obtained by modifying the surface of a mother particle illustrated in Fig. 1. Fig. 2(a) shows an example characterized as supporting micro-particles 21 of silica or the like on its surface. Fig. 2(b) shows another example  
25        characterized as having a single molecular layer 22 on its surface. Fig. 2(c) shows still another example characterized as having indentations 23 formed on its surface. Fig. 2(d) shows a mother particle comprised of an outer shell 24 with a hollow internal space 25 which may be filled with a core material or left empty. The outer shell may comprise a polymer material or a metal. The core material may comprise a solid such as a metal or a  
30        polymer material. The hollow internal space 25 may be filled with a gas or a liquid. Fig.

2(e) shows another mother particle comprising composite particles structured as a hollow polymer 26 containing therein one or more micro-capsules.

Fig. 3 shows mother particles according to this invention in different shapes, Fig. 3(a) showing a spherical shape with two axes of symmetry, Figs. 3(b), 3(c) and 3(d) showing cylindrical shapes with one axis of symmetry, and Fig. 3(e) showing a composite of two spherical parts.

Polishing agents embodying this invention as described above may be produced by adding mother particles to very fine abrading particles and stirring them together.

A polishing method embodying this invention is characterized as comprising the steps of supplying a specified amount of a polishing agent according to this invention between a target object to be polished and a polishing means and causing the polishing means to undergo a movement relative to the target object while in contact therewith. During this process, these very fine abrading particles are believed to remain attached to the surfaces of the mother particles by the electrostatic, van der Waals or mechanical force.

Examples of the aforementioned polishing means include tapes and lapping plates. Flat and smooth tapes are preferred for this purpose, such as PET tapes. Flat and smooth lapping plates made of a metallic material such as copper and tin or a ceramic or plastic material may be suitably used. The lapping plate need not have a flat surface but may have a curved polishing surface such as a spherical surface or an uneven surface with indentations and protrusions. With the use of such a plate, prior art polishing pads such as comprising urethane as well as tapes become dispensable, and the problems related to flatness and small-scale evenness can be properly addressed to.

A polishing agent of this invention is preferably supplied at a rate of 1-100cc/min, and preferably 20-50cc/min. When a lapping process is carried out on the target object 1 while rotating the lapping plate 2, the speed of rotation is 10-10000rpm, and preferably 100-1000rpm.

Test experiments are explained next in order to more clearly describe the invention. In these test examples, micro-polymers were used as micro-beads.

As very fine abrading particles according to this invention, use was made of colloidal silica (Snowtex 30 (pH 10.5) produced by Nissan Kagaku Kabushiki Kaisha) of which specifications are given below in Table 1.

5 Table 1

|   |                        |
|---|------------------------|
| Content of anhydrous silicic acid (SiO <sub>2</sub> ) | 30-31 weight %         |
| Content of sodium oxide (Na <sub>2</sub> O)           | Less than 0.6 weight % |
| Concentration of hydrogen ion                         | pH 9.0-10.5            |
| Particle diameters                                    | 10-20nm                |
| Viscosity at 25°C                                     | Less than 6mP          |
| Specific weight at 20°C                               | 1.20-1.22              |

As mother particles (micro-polymers) according to this invention, use was made of two kinds of benzoguanamine resin (Epostar L15 and Epostar MS produced by Nippon Shokubai Kabushiki Kaisha) of which specifications are given below respectively in

10 Tables 2 and 3. Fig. 4(a) is an SEM (scanning electron microscope) photograph of original powder of Epostar L15, and Fig. 4(b) is its enlargement. A small amount of residual silica is discernible on the surface of micro-polymer.

Table 2

| Constituent                                | Benzoanamine-formaldehyde resin  | Silica           | Nonion surfactant |
|--|--|------------------|-------------------|
| Content                                    | 94%  | 5%               | 1%                |
| Chemical formula                           | (C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> •CH <sub>2</sub> O) <sub>2</sub> | SiO <sub>2</sub> |                   |
| Reference Number in Government Publication | (7)-555  | (1)-548          | 7-559             |
| Diameter of spherical shape                | Average diameter = 10-20μm;<br>Maximum = 30μm; Minimum = 8μm                   |                  |                   |

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Table 3

| Constituent                                | Benzoanamine-formaldehyde resin  | Silica  | Nonion surfactant |
|--|--|---------|-------------------|
| Content                                    | 89.8%  | 10%     | 1%                |
| Chemical formula                           | $(C_9H_9N_5 \cdot CH_2O)_2$  | $SiO_2$ |                   |
| Reference Number in Government Publication | (7)-555  | (1)-548 | 7-559             |
| Diameter of spherical shape                | Average diameter = 1-3 $\mu$ m;<br>Maximum = 10 $\mu$ m; Minimum = 0.5 $\mu$ m |         |                   |

Micro-polymers described above were added into colloidal silica described above with stirring. Composition of the polishing agent thus produced in this example was as shown in Table 4. Fig. 4(c) is an SEM photograph of this polishing agent (Epostar L15 + colloidal silica) after being dried. Fig. 4(d) is its enlargement, showing colloidal silica attached approximately evenly on the surface of Epostar L15 powder.

Table 4

|                  |                  |
|------------------|------------------|
| Micro-polymer    | 0.5-5 weight %   |
| Colloidal silica | 5-10 weight %    |
| Pure water       | 85-94.5 weight % |

A plane polishing process was carried out on a 4-inch silicon wafer by using a plane polishing disc produced by Okamoto Kikai Co. The applied pressure was 300gf/cm<sup>2</sup>, the diameter of the lapping plate was 260mm, the rotary speed of the lapping plate was 64rpm, the polishing agent was added at the rate of 25cc/min and the processing time was 20 minutes. Fig. 4(e) is an SEM photograph of the micro-polymer slurry after the polishing process and Fig. 4(f) is its enlargement, showing colloidal silica removed from portions of the surface of the micro-polymer because of the polishing process.

By this polishing process according to the present invention, surface roughness of  $R_a=2.0-2.5nm$  could be accomplished. This is comparable to the result of polishing by using a normal IC1000 polishing pad with colloidal silica. This means that the present invention is capable of bringing about an improvement in the polishing efficiency by about 20-50% over the prior art methods. It was also ascertained that the torque on the

lapping plate (that is, the displacement resistance of the target object being polished with respect to the lapping plate with the presence of the micro-polymer slurry in between) was reduced by 20-30%. In other words, a smaller power source can be used and the device can be miniaturized accordingly.